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(71) Applicant (for all designated States except US): RE-FRIGERANT PRODUCTS LTD. [GB/GB]; N9 Central Park Estate, Westinghouse Road, Trafford Park, Manchester M17 1PG (GB).

(72) Inventors; and
(75) Inventors/Applicants (for US only): POWELL, Richard [GB/GB]; 9 Sadlers Wells, Bunbury, Cheshire CW6 9NW (GB). POOL, John, Edward [GB/GB]; Wynthorpe, Murieston Road, Hale, Altrincham, Cheshire WA15 9ST (GB). CAPPER, John, Derek [GB/GB]; 45 Grove

Mount, Davenham, Northwich, Cheshire CW9 8LY (GB). THOMAS, James, Victor [CA/CA]; 247 Howe Avenue, Fall River, Nova Scotia B2T 1H7 (CA).

(74) Agent: BROWNE, Robin, Forsythe; Urquhart-Dykes & Lord, Tower House, Merrion Way, Leeds LS2 8PA (GB).

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(54) Title: R 22 REPLACEMENT REFRIGERANT

(57) Abstract: A refrigerant composition comprising a hydrofluorocarbon component including 1,1,1,2-tetrafluoroethane (HCFC 134a), the composition further comprising an additive selected from a saturated hydrocarbon or mixture thereof boiling in the range -5 to +70 °C.

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R 22 REPLACEMENT REFRIGERANT

This invention relates to a refrigerant particularly but not exclusively for air conditioning systems. The system relates especially to refrigerant compositions which have no adverse effect on the atmospheric ozone layer and to compositions which can be added to existing refrigerants which are compatible with lubricants commonly used in refrigeration and air conditioning systems. The invention also relates to a method of modifying refrigeration and air conditioning systems.

Chlorofluorocarbons (CFCs) eg CFC 11 and CFC 12 are stable, of low toxicity and non-flammable providing low hazard working conditions used in refrigeration and air conditioning systems. When released they permeate into the stratosphere and attack the ozone layer which protects the environment from damaging effects of ultraviolet rays. The Montreal Protocol, an International environmental agreement signed by over 160 countries, mandates the phase-out of CFCs according to an agreed timetable. This now includes hydrochlorofluorocarbons (HCFCs) which also have an adverse effect on the ozone layer.

R 22 is a chemical fluid and by far the largest HCFC refrigerant used globally in refrigeration and air conditioning equipment. R 22 has an Ozone Depletion Potential (ODP) of approximately 5% of CFC 11. After CFCs have been phased out, the chlorine content of R 22 will make it the largest ozone depleting substance in volumetric terms. R 22 is also the subject of a phase-out schedule under the Montreal Protocol. R 22 is prohibited from use in new equipment in some countries.

Any replacement for HCFC 22 must have no ability to deplete ozone. The compositions of the present invention do not include chlorine atoms and consequently they will have no deleterious effect on the ozone layer while providing a similar performance as a working fluid to R 22 in refrigeration apparatus.

Various terms have been used in patent literature to describe refrigerant mixtures. These may be defined as follows:

Zeotrope: A fluid mixture whose vapour and liquid compositions are different at a specified temperature.

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Temperature glide: If a zeotropic liquid is distilled at constant pressure its boiling point will increase. The change in boiling point from the beginning of the distillation until the point when a liquid phase has just disappeared is called the temperature glide. A glide is also observed when the saturated vapour of a zeotrope is condensed at constant pressure.

Azeotrope: A fluid mixture of specified composition whose vapour and liquid compositions are the same at a specified temperature. Strictly speaking a fluid mixture which is an azeotrope under for example evaporator conditions, cannot also be an azeotrope under the condenser conditions. However the refrigeration literature may describe a mixture as azeotropic provided that it meets the above definition at some temperature within its working range.

Near-azeotropes: A blend which boils over a small temperature range, that has a small temperature glide.

Retrofit refrigerant mixture: A non-chlorine-containing mixture used to replace completely the original CFC or HCFC refrigerant.

Extender refrigerant mixture: A non-chlorine-containing mixture added during servicing to the HCFC refrigerant remaining in a unit, that is a top up refrigerant to make good any leakage.

Hermetic compressor: A compressor where the electric motor is in the same totally welded casing as the compressor. The motor is cooled by the refrigerant vapour returning to the compressor. The heat generated by the motor is removed through the condenser.

Semi-hermetic compressor: Similar to a hermetic compressor, the major difference being the casing has a bolted joint which can be opened to enable the motor and compressor to be serviced.

Open compressor: A compressor which is driven by an external motor via a drive shaft passing through the compressor casing. The motor heat is dissipated directly to the environment, not via the condenser. This results in a slightly more efficient performance than a hermetic compressor, but refrigerant leaks can occur at the shaft seal.

Percentages and proportions referred to in this specification are by weight unless indicated otherwise. Percentages and proportions are selected to total 100%. HFC and HCFC refrigerant compounds are referred to below by the letter R.

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According to a first aspect of the present invention a refrigerant composition comprises 1,1,1,2-tetrafluoroethane (R134a), pentafluoro ethane (R 125) and an additive selected from a saturated hydrocarbon or mixture thereof boiling in the range –5 to +70°C; wherein the of weights of R 125 and R 134a are in the ranges:

R 125	50 - 80%
R 134a	50 - 20%

The compositions may be used as retrofit refrigerant mixtures. The composition may also be used as extenders as discussed below. The compositions may be used in semi-hermetic and hermetic systems.

The preferred weights of R125 to R 134a are in the ranges:

R 125	60 - 80%
R 134a ·	40 - 20%

A more preferred range is:

R 125	60 - 78%
R 134a	40 - 22%

A most preferred range is:

R 125	64 - 76%
R 134a	34 - 24%

These ranges are preferred for hermetic and semi-hermetic systems. The composition may also be used in an open system. The preferred weights in an open system are in the ranges:

R 125	57 - 78%
R 134a	43 - 22%.

A more preferred range is:

R 125	63 - 76%
R 134a	33 - 24%

The proportion of R 125 used in an open system may be up to 10%, preferably 4 to 5 % higher than in a hermetic or semi-hermetic system.

In a first aspect of this invention no other refrigerant may be included in the mixture. In a second aspect, suitable for use as an R 22 extender, an additional refrigerant R 32 may be added.

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Preferred hydrocarbons additives are selected from the group consisting of: 2-methylpropane, 2,2-dimethylpropane, butane, pentane, 2-methylbutane, cyclopentane, hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and methylcyclopentane. The hydrocarbon additive preferably has a boiling point in the range 20 to 40°C. Use of n-pentane, cyclopentane, iso-pentane and mixtures thereof is preferred. Use of n-pentane, isopentane or mixtures thereof is especially preferred. Commercially available saturated hydrocarbon mixtures are available from cyclopentane commercial grade from Phillips Petroleum International NV, Norpar ʳ5 S n-pentane from Exxon Chemical and iso-pentane Q1111 from Shell Chemicals.

Relative proportions of the pentane and butane components may be selected to give a total of 0.2 to 5% of the compositions, preferably 2 to 4%, more preferably 3 to 4%. An amount of pentane, preferably isopentane of 0.2 to 2% may be used together with a corresponding amount of 4.8 to 3% of butane in a composition containing a total of 5% hydrocarbon. In compositions with less than 5% hydrocarbon, for example 1% or 4%, relatively larger ratios of butane : pentane may be employed to minimise hydrocarbon build-up on leakage. Flammability risks are therefore reduced.

According to a second aspect of the present invention a refrigerant extender mixture comprises a composition in accordance with the first aspect of this invention.

According to a third aspect of this invention a refrigerant composition comprises a composition in accordance with the first aspect of this invention together with R 22. This invention also provides a method of modifying a refrigerator or air conditioning system incorporating R 22 as refrigerant, the method comprising the step of adding a composition in accordance with the second aspect of this invention to the refrigerant of the system.

Positive displacement compressors, that is reciprocating or rotary compressors, used in refrigeration systems suck in small amounts of lubricant from the crank case which are ejected with the refrigerant vapour through the exhaust valves. In order to maintain compressor lubrication this oil must be forced around the circuit by the refrigerant stream and returned to the crank case. CFC and HCFC refrigerants are miscible with hydrocarbon oils and hence carry the oils around the circuit. However HFC refrigerants and hydrocarbon lubricants have low mutual solubilities so effective oil return may not occur. The problem is particularly acute in evaporators where low temperatures can increase the

viscosities of oils sufficiently to prevent them being carried along the tube walls. With CFCs and HCFCs enough refrigerant remains in the oil to reduce the viscosities to enable oil return to occur.

When using HFCs with hydrocarbon lubricants oil return can be facilitated by introducing into the system a hydrocarbon fluid having the following properties:

(a)   sufficient solubility in the lubricant at the evaporator temperature to reduce its viscosity; and

(b)   sufficient volatility to allow distillation from the hot lubricant in the compressor crank case.

Hydrocarbons fulfil these requirements.

Refrigerant compositions in accordance with this invention confer several advantages. R 125 has fire suppressing characteristics. The presence of R125 suppresses the flammability of the refrigerant mixture. The higher HFC content enables more n-pentane to be added to the mixture thereby improving the solubility properties of the mixture with traditional lubricants, for example mineral and alkyl benzene oils.

The present invention may confer a number of benefits in comparison to R 22 including zero ozone depletion, lower discharge temperature, and higher capacity.

The present invention may confer a number of benefits in comparison to the HFC replacement R407C including superior hydrocarbon oil return, better motor cooling in hermetic compressors, lower discharge temperature and lower discharge pressure.

The invention is further described by means of examples but not in any limitative sense.

EXAMPLE 1

The performances of five R125/R134a/pentane compositions were evaluated using standard refrigeration cycle analysis techniques in order to assess their suitability as retrofit replacements for R22 in hermetic or semi-hermetic systems. The operating conditions, used for the analyses were chosen as being typical of those conditions that are found in air conditioning systems. Since the blends were zeotropes the midpoints of their temperature glides in the evaporator and condenser were chosen to define the temperature

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limits of the cycle. The same temperatures were also used to generate performance data for R22.

The pentane was present at 4% by weight based on the total weight of the R125/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following refrigerant compositions were subjected to cycle analysis:

1. A composition comprising 44% R125: 56% R134a
2. A composition comprising 56% R125: 44% R134a
3. A composition comprising 64% R125: 36% R134a
4. A composition comprising 76% R125: 24% R134a
5. A composition comprising 80% R125: 20% R134a

The following cycle conditions were used in the analysis:

COOLING DUTY DELIVERED   10 kW

EVAPORATOR

Midpoint fluid evaporation temperature   7.0 °C

Superheating   5.0 °C

Suction line pressure drop (in saturated temperature)   1.5 °C

CONDENSER

Midpoint fluid condensing temperature   45.0 °C

Subcooling   5.0 °

Exhaust line pressure drop (in saturated temperature)   1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficient   0.3

COMPRESSOR

Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER

Indoor fan	0.3 kW
Outdoor fan	0.4 kW
Controls	0.1 kW

The results of analysing the performances in an air-conditioning unit using these operating conditions are shown in Table 1. For comparison the performance of R22 is also shown.

All compositions have lower exhaust temperatures than R22 and are therefore superior on this account. However composition 5 is not preferred because the exhaust pressure is more than 2 bar above that of R22. Composition 1 is unacceptable because the refrigerant capacity is less than 90% of that of R22. The overall performances of compositions 2, 3 and 4 meet the criteria set out above and therefore satisfy the requirements of this invention.

EXAMPLE 2

The performances of five R125/R134a/pentane compositions were evaluated using standard refrigeration cycle analysis techniques in order to assess their suitability as retrofit replacements for R22 in open systems. The operating conditions, used for the analyses were chosen as being typical of those conditions that are found in air-conditioning systems. Since the blends were zeotropes the midpoints of their temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

The pentane was present at 4% by weight based on the total weight of the R125/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following refrigerant compositions were subjected to cycle analysis:

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1.   A composition comprising 44% R125: 56% R134a

2.   A composition comprising 56% R125: 44% R134a

3.   A composition comprising 64% R125: 36% R134a

4.   A composition comprising 76% R125: 24% R134a

5.   A composition comprising 80% R125: 20% R134a

The following cycle conditions were used in the analysis:

COOLING DUTY   10 kW

EVAPORATOR

Midpoint fluid evaporation temperature   7.0 °C

Superheating   5.0 °C

Suction line pressure drop (in saturated temperature)   1.5 °C

CONDENSER

Midpoint fluid condensing temperature   45.0 °C

Subcooling   5.0 °C

Exhaust line pressure drop (in saturated temperature)   1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficiency   0.3

COMPRESSOR

Electric motor efficiency   0.85

Compressor isentropic efficiency   0.7

Compressor volumetric efficiency   0.82

PARASITIC POWER

Indoor fan   0.3 kW

Outdoor fan   0.4 kW

Controls   0.1 kW

The results of analysing the performances in an air-conditioning unit using these operating conditions are shown in Table 2. For comparison the performance of R22 is also shown.

All compositions have lower exhaust temperatures than R22 and are therefore superior on this account. However composition 5 is unacceptable because its exhaust pressure is more than 2 bar above that of R22. Compositions 1 and 2 are unacceptable because their refrigerant capacities are less than 90% of that of R22. The overall performances of compositions 3 and 4 meet the criteria set out above and therefore satisfy the requirements of this invention.

EXAMPLE 3

The performances of five R125/R134a/pentane compositions were evaluated using standard refrigeration cycle analysis techniques the in order to assess their suitability as retrofit replacements for R22 in hermetic or semi-hermetic systems not fitted with a liquid line/suction line heat exchanger. The operating conditions, used for the analyses were chosen as being typical of those conditions that are found in air conditioning systems. Since the blends were zeotropes the midpoints of their temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

The pentane was present at 4% by weight based on the total weight of the R125/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following refrigerant compositions were subjected to cycle analysis:

1.   A composition comprising 44% R125: 56% R134a

2.   A composition comprising 56% R125: 44% R134a

3.   A composition comprising 64% R125: 36% R134a

4.   A composition comprising 76% R125: 24% R134a

5.   A composition comprising 80% R125: 20% R134a

The following cycle conditions were used in the analysis:

COOLING DUTY	10 kW

EVAPORATOR	
Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperate	1.5 °C

CONDENSER	
Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

COMPRESSOR	
Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER	
Indoor fan	0.47 kW
Outdoor fan	0.26 kW
Controls	0.1 kW

The results from analysing the performances in an air-conditioning unit using these operating conditions are shown in Table 3. For comparison the performance of R22 is also shown.

All compositions have lower exhaust temperatures than R22 and are therefore superior on this account. However composition 5 is unacceptable because its exhaust pressure is more than 2 bar above that of R22. Compositions 1 and 2 are unacceptable because their refrigerant capacities are less than 90% of that of R22. The overall performances of compositions 3 and 4 meet the criteria set out above and therefore satisfy the requirements of this invention.

EXAMPLE 4

The performances of two R125/R134a/pentane compositions were evaluated using standard refrigeration cycle analysis techniques in order to assess their suitability as extenders for R22 in hermetic or semi-hermetic systems. The operating conditions selected for the analyses are typical of those conditions found in air conditioning systems. Since the blends were zeotropes the midpoints of their temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle and were also used to generate the performance of R22 for comparison.

The pentane was present at 4% by weight based on the total weight of the R125/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following R22 extender compositions were subjected to cycle analysis:

1.   A composition comprising 64% R125: 36% R134a.

2.   A composition comprising 44% R125: 56% R134a.

To establish the effects on unit performance resulting from successive dilutions of R22 by the above extenders the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are summarised in Tables 4a and 4b. Key parameters are plotted in Chart 1 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

COOLING DUTY   10 kW

EVAPORATOR .

Midpoint fluid evaporation temperature   7.0 °C

Superheating   5.0 °C

Suction line pressure drop (in saturated temperature)   1.5 °C

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CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE

Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER

Indoor fan	0.3 kW
Outdoor fan	0.4 kW
Controls	0.1 kW

All compositions have lower exhaust temperatures than R22 and are therefore superior on this account.

Composition 1 provides a cooling capacity greater than 90% of that of R22 over the whole of the dilution range. Blends containing more than 45% R22 have capacities equal to or better than that of R22. The COP (system) is within 2% of that of R22 over the whole of the dilution range. This composition therefore meets the requirements of this invention.

Composition 2 provides a cooling capacity greater than that 90% of R22 for blends containing down to 20% of R22. Its COP (system) is essentially the same as that of R22 over the whole of the dilution range. This composition therefore meets the requirements of this invention for blends containing down to 20% R22.

EXAMPLE 5

An R32/R134a/pentane composition was evaluated using standard refrigeration cycle analysis techniques to assess its suitability as an extender for R22 in hermetic or

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semi-hermetic systems. The operating conditions selected for the analysis are typical of those conditions found in air conditioning systems. Since the blend was a zeotrope the midpoints of its temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

The pentane was present at 4% by weight based on the total weight of the R32/R134a blend. To simplify the calculation this small amount of pentane was omitted.

The following R22 extender composition was subjected to cycle analysis: A composition comprising 44% R125 by weight, 56% by weight R134a.

To establish the effect on unit performance resulting from successive dilutions of R22 by topping up with the above extender the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are shown in Table 5 and the results plotted out in Chart 2 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

EVAPORATOR

Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperature)	1.5 °C

CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficiency	0.3

COMPRESSOR

Electric motor efficiency	0.85
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

PARASITIC POWER

Indoor fan	0.3 kW
Outdoor fan	0.4 kW
Controls	0.1 kW

All blends containing the extender have lower exhaust temperatures than R22 and therefore meet the requirements of this specification. The COP (system) is essentially equal to that of R22 over the whole of the dilution range. The cooling capacity of the refrigerant is not less than 98% of that of R22 over the whole of the dilution range. For dilutions down to 20% of R22 the capacity is equal to or greater than that of R22. The exhaust pressure is less than the 0.5 bar above that of R22 over the whole of the dilution range.

The results of analysing the performance of an air-conditioning unit using these operating conditions are shown in Table 5.

R32/R134a 30/70 therefore meets the requirements of this invention.

EXAMPLE 6

An R32/R125/R134a/pentane composition was evaluated using standard refrigeration cycle analysis techniques program to assess its suitability as an extender for R22 in hermetic or semi-hermetic systems. The operating conditions selected for the analysis are typical of those conditions found in air conditioning systems. Since the blend was a zeotrope the midpoints of its temperature glides in the evaporator and condenser were chosen to define the temperature limits of the cycle. The same temperatures were also used to generate performance data for R22.

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The pentane was present at 4% by weight based on the total weight of the R32/R134a blend.

To simplify the calculation this small amount of pentane was omitted.

The following R22 extender composition was subjected to cycle analysis:

A composition comprising 23% by weight of R 32, 25%R125 by weight and 52% by weight R134a.

To establish the effect on unit performance resulting from successive dilutions of R22 by topping up with the above extender the cycle was analysed for refrigerant compositions containing mass fractions of R22 from 1.0 down to 0.0. The results are shown in Table 6 and the results plotted out in Chart 3 with the calculated points connected by smooth curves.

The following cycle conditions were used in the analysis:

EVAPORATOR

Midpoint fluid evaporation temperature	7.0 °C
Superheating	5.0 °C
Suction line pressure drop (in saturated temperature)	1.5 °C

CONDENSER

Midpoint fluid condensing temperature	45.0 °C
Subcooling	5.0 °C
Exhaust line pressure drop (in saturated temperature)	1.5 °C

LIQUID LINE/SUCTION LINE HEAT EXCHANGER

Efficiency	0.3

COMPRESSOR

Electric motor efficiency	0.8
Compressor isentropic efficiency	0.7
Compressor volumetric efficiency	0.82

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PARASITIC POWER

Indoor fan	0.3
Outdoor fan	0.4 kW
Controls	0.1 kW

The results of analysing the performance of an air-conditioning unit using these operating conditions are shown in Table 6.

All blends containing the extender have lower exhaust temperatures than R22 and therefore meet the requirements of this specification. The COP (system) is not less than 98% of that of R22 over the whole of the dilution range. The cooling capacity of the refrigerant is greater than of that of R22 over the whole of the dilution range. The exhaust pressure is less than the 2.0 bar above that of R22 over the whole of the dilution range.

R32/R134a in the ratio 30/70 therefore meets the requirements of this invention.

EXAMPLE 7

Refrigerant compositions comprising R 125, R 134a and hydrocarbon mixtures in commercial heat pump applications were assessed using a Comfort Aire model PHEC-60-1a 5 ton rooftop heat pump with a nominal cooling capacity of 56,000 btu and nominal heating capacity of 56,000 btu. An oil sight-glass was installed on the hermetic compressor and temperature sensors were installed on the suction and discharge lines and on the liquid line. Suction and discharge gauges were also installed.

The system was operated in both the cooling and heating mode with R 22 and the following data was recorded: voltage, amperage, suction pressure, suction temperature, discharge pressure, discharge temperature, liquid line temperature, evaporator temperature, ambient temperature, oil level and return supply air temperature. The R 22 charge was recovered and replaced successively with blends 1 to 6 of the following compositions.

	R-125	R-134a	Pentane	Isopentane	Butane
Blend #1	64%	34%	2%		
Blend #2	70%	28%	2%		
Blend #3	55%	43%	2%		
Blend #4	60.5%	37.5%	2%		
Blend #5	45%	52%		1%	2%
Blend #6	55%	42%		1%	2%

It was observed that oil return was similar to R 22 operating levels with all of the
blends employed, indicating that pentane and isopentane/butane additives provided proper
oil return. Some blends required addition of up to 20% refrigerant to prevent icing of the
evaporator. Capacities were found to vary with the composition employed. The energy
consumption was generally lower with all blends. Discharge pressures were slightly
higher on average with blends that exceeded 60.5% R 125 and lower with blends
containing less than 60.5% R 125. The suction pressures and discharge temperatures were
lower with all blends used. The superheat measured at the evaporator outlet was much
higher than R 22 and the temperature difference across the evaporator was generally
greater in the cooling mode and less in the heating mode. It was noted that pentane and
isopentane/butane additives provided the necessary oil return. Blends #3, 5 and 6 provided
the closest similarities to R 22 operational temperatures and pressures.

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CLAIMS

1.   A refrigerant composition comprising 1,1,1,2-tetrafluoroethane (R 134a), pentafluoroethane (R 125) and an additive selected from a saturated hydrocarbon or mixture thereof boiling in the range –5 to +70°C; wherein the weights of R 125 to R 134a is in the ranges:

            R 125   50 - 80%
            R 134a   50 - 20%

2.   A refrigerant composition as claimed in claim 1, wherein the weights are in the ranges:

            R 125   60 - 80%
            R134a   40 - 20%

3.   A refrigerant composition as claimed in claim 2, wherein the weights are in the ranges:

            R 125   60 - 78%
            R 134a   40 - 22%

4.   A refrigerant composition as claimed in claim 3, wherein the weights are in the ranges:

            R 125   64 - 76%
            R 134a   36 - 24%

5.   A refrigerant composition as claimed in claim 1, wherein the weights are in the ranges:

            R 125   57 - 78%
            R 134a   43 - 22%

6.   A refrigerant composition as claimed in claim 5, wherein the weights are in the ranges:

            R 125   63 - 76%
            R 134a   37 - 24%

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7.   A refrigerant composition as claimed in any preceding claim, wherein the hydrocarbon additive is selected from the group consisting of 2-methylpropane, 2,2-dimethylpropane, butane, pentane, 2-methylbutane, cyclopentane, hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethybutane, methylcyclopentane and mixtures thereof.

8.   A refrigerant composition as claimed in any preceding claim, wherein the hydrocarbon additive has a boiling point in the range of 20 to 40°C.

9.   A refrigerant composition as claimed in claim 8, wherein the hydrocarbon additive is selected from: n-pentane, cyclopentane, iso-pentane and mixtures thereof.

10.   A refrigerant composition as claimed in claim 9, wherein the hydrocarbon additive is n-pentane.

11.   A refrigerant composition as claimed in claim 9 or 10, wherein the additive further comprises butane.

12.   A refrigerant compositions as claimed in claim 11, wherein the ratio of pentane : butane is 1 : 3 to 1 : 8, preferably about 1 : 5.

13.   A refrigerant composition as claimed in any preceding claim, wherein the amount of hydrocarbon additive is from a trace to 10%.

14.   A refrigerant composition as claimed in claim 13, wherein the amount of hydrocarbon additive is 1 to 8%.

15.   A refrigerant composition as claimed in claim 14, wherein the amount of hydrocarbon additive is 2 to 4%.

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16.   A refrigerant composition as claimed in any of claims 1 to 15 together with a proportion of R 22.

17.   A refrigerant extender mixture comprising a refrigerant composition as claimed in any preceding claim.

18.   A method of modifying a refrigerator or air conditioning system which incorporates R 22 as refrigerant, the method comprising the step of adding a refrigerant extender as claimed in claim 17 to the refrigerant of the system.

19.   Use of a refrigerant composition as an extender to R 22, wherein the hydrofluorocarbon component comprises R 32, R 125 and R 134a wherein the ratio of weights of R 32, R 125 and R 134a are in the ranges:

R 32	18 - 28%
R 125	20 - 30%
R 134a	42 - 62%

Table 1

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	104.68	79.75	78.51	77.60	76.07	75.51
COP (system)	2.49	2.50	2.47	2.45	2.41	2.40
Capacity (kW/m³)	3066	2581	2747	2862	3041	3102
Glide in evaporator (°C)	0	3.06	3.17	3.03	2.47	2.19
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

Table 2

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	92.9	72.8	71.9	71.2	70.1	69.7
COP (system)	2.59	2.57	2.54	2.52	2.48	2.47
Capacity (kW/m^3)	3222	2669	2838	2956	3138	3200
Glide in evaporator (°C)	0	3.06	3.17	3.03	2.47	2.19
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

Table 3

Refrigerant % by weight	R-22	1. 125/134a 44/56	2. 125/134a 56/44	3. 125/134a 64/36	4. 125/134a 76/24	5. 125/134a 80/20
Discharge pressure (bar)	17.91	15.89	17.19	18.13	19.68	20.23
Discharge temperature (°C)	94.63	71.81	70.63	69.71	68.082	67.47
COP (system)	2.45	2.42	2.39	2.37	2.33	2.36
Capacity (kW/m³)	3077	2535	2692	2800	2965	3021
Glide in evaporator (°C)	0	2.88	2.99	2.87	2.34	2.07
Glide in condenser (°C)	0	2.97	2.94	2.71	2.09	1.81

Table 4a R125/R134a 64%/36% as Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	18.13	18.47	18.69	18.81	18.84	18.80	18.70	18.56	18.37	18.15	17.91
Discharge temperature (°C)	77.6	79.7	81.8	84.0	86.4	89.0	91.7	94.6	97.8	101.1	104.7
COP (system)	2.45	2.45	2.46	2.46	2.47	2.47	2.48	2.48	2.49	2.49	2.49
Capacity (kW/m^3)	2862	2937	2996	3042	3074	3096	3107	3108	3101	3087	3069
Glide in evaporator (°C)	3.03	2.91	2.66	2.36	2.04	1.73	1.41	1.08	0.75	0.39	0
Glide in condenser (°C)	2.71	2.55	2.31	2.06	1.80	1.54	1.28	1.09	0.71	0.38	0

Table 4b R125/R134a 44%/56% as Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	15.90	16.41	16.83	17.17	17.44	17.64	17.79	17.88	17.93	17.93	17.91
Discharge temperature (°C)	79.6	81.7	83.7	85.8	88.0	90.3	92.8	95.5	98.3	101.4	104.7
COP (system)	2.50	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
Capacity (kW/m³)	2581	2675	2756	2825	2885	2935	2977	3010	3036	3054	3066
Glide in evaporator (°C)	3.06	3.08	2.91	2.62	2.27	1.89	1.50	1.12	0.74	0.37	0
Glide in condenser (°C)	2.97	2.89	2.66	2.36	2.02	1.69	1.34	1.00	0.67	0.34	0

Table 5 R32/134a 30/70 as an Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	18.08	18.18	18.27	18.33	18.36	18.36	18.34	18.28	18.19	18.07	17.91
Discharge temperature (°C)	98.0	98.4	98.9	99.3	99.8	100.4	101.0	101.8	102.6	103.6	104.7
COP (system)	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
Capacity (kW/m^3)	3030	3049	3066	3080	3091	3098	3101	3100	3094	3083	3066
Glide in evaporator (°C)	5.03	4.59	4.12	3.62	3.11	2.59	2.07	1.55	1.03	0.51	0
Glide in condenser (°C)	5.13	4.62	4.11	3.60	3.08	2.57	2.07	1.56	1.06	0.54	0

Table 6 R32/125/134a 23/25/52 as an Extender for R22

Refrigerant % R22 by weight	0	10	20	30	40	50	60	70	80	90	100
Discharge pressure (bar)	19.30	19.32	19.30	19.25	19.16	19.03	18.87	18.68	18.45	18.20	17.91
Discharge temperature (°C)	92.5	93.3	94.1	95.0	96.0	97.1	98.4	99.7	101.2	102.9	104.7
COP (system)	2.47	2.47	2.47	2.47	2.47	2.48	2.48	2.48	2.49	2.49	2.49
Capacity (kW/m³)	3172	3183	3190	3193	3191	3183	3171	3157	3129	3101	3066
Glide in evaporator (°C)	4.8	4.4	3.9	3.4	2.9	2.4	1.9	1.5	1.0	0.5	0
Glide in condenser (°C)	4.7	4.2	3.8	3.3	2.8	2.4	1.9	1.5	1.0	0.5	0

TABLE 7

COMMERCIAL ROOF TOP HEAT PUMP 5 TON

	R-22	BLEND 1	BLEND 3	BLEND 4	BLEND 5	BLEND 6	BLEND 7
WT% COMPOSITION		64/34/2	70/28/2	55/43/2	60.5/37.5/2	45/52/1/2	55/42/1/2
COOLING MODE							
ADDITIONAL REFR. REQ'D		.9 KG	.9 KG	NONE	.9 KG	NONE	NONE
SUCTION PRESSURE	4.48	3.5	3.37	3.03	3.45	2.69	3.1
SUCTION TEMPERATURE	18	22	19.4	27	20	22	21.7
DISCHARGE PRESSURE	13.1	13.5	13.17	12.68	12.42	11.25	12.42
DISCHARGE TEMP.	90	80	73	81	72	76	76
LIQ. LINE TEMP.	31	29	26	32	26	26	26
AMBIENT TEMPERATURE	22	24	21.7	26	21.2	22	22
OIL LEVEL	10.8CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM
AMPERAGE	22.27	19.86	19.64	17.72	19.06	16.13	17.83
VOLTAGE	200	201	199	200	199	203	200
EVAPORATOR TEMP.	7.2	3.9	2.2	4	5	1.7	2.3
AIR TEMP. DIFFERENCE	12.2	17.7	16.1	19.7	14.4	17.3	16.1
SUPERHEAT	9.1	21	19.4	28	20	26	23.3
HEATING MODE							
SUCTION PRESSURE	4.82	4.97	4.9	3.6	4.69	3.45	3.72
SUCTION TEMP.	25	23	23	26	22	23	22
DISCHARGE PRESSURE	20.34	25.5	25.6	19.3	24	17.94	19.3
DISCHARGE TEMP.	120	98	98	95	94	91	91
LIQ. LINE TEMP.	32.2	30	30	32	29	27	26
AMBIENT TEMP.	24.2	24	22.2	25	22.4	22	20
OIL LEVEL	10.8CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM	10.8 CM
AMPERAGE	28.97	28.08	27.63	21.9	26.72	20.77	22.54
VOLTAGE	198	199	198	199	198	203	199
EVAPORATOR TEMP.	41	36.2	36.1	36.1	34	32	31
AIR TEMP. DIFFERENCE	11.1	7.8	7.8	6.3	7.6	7.2	7.5
SUPERHEAT	NA	NA	NA	NA	NA	NA	NA

PRESSURES ARE IN BARS GAUGE PRESSURE
TEMPERATURES ARE IN CELSIUS
ALL READINGS ARE AVERAGES OVER SEVERAL HOURS OF OPERATION
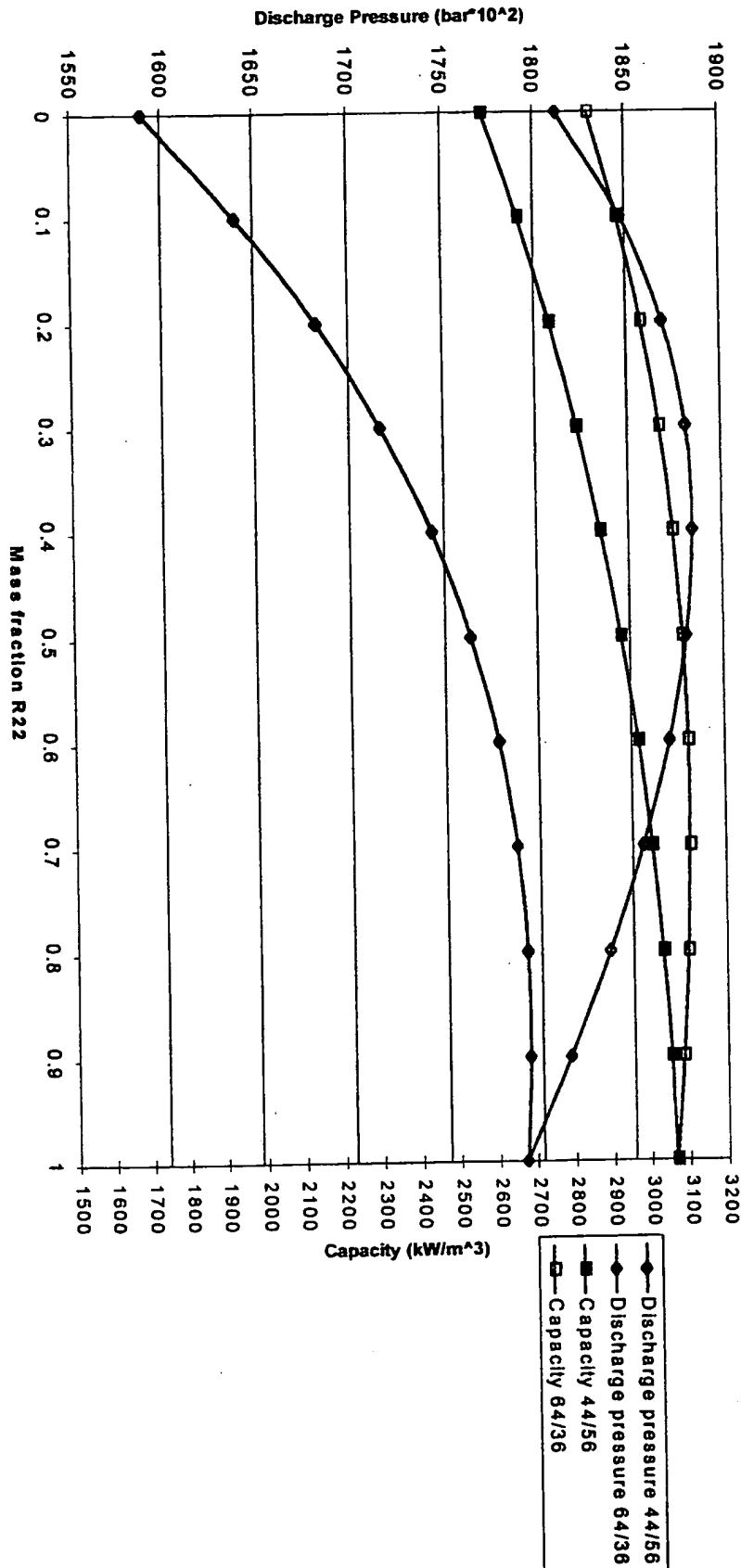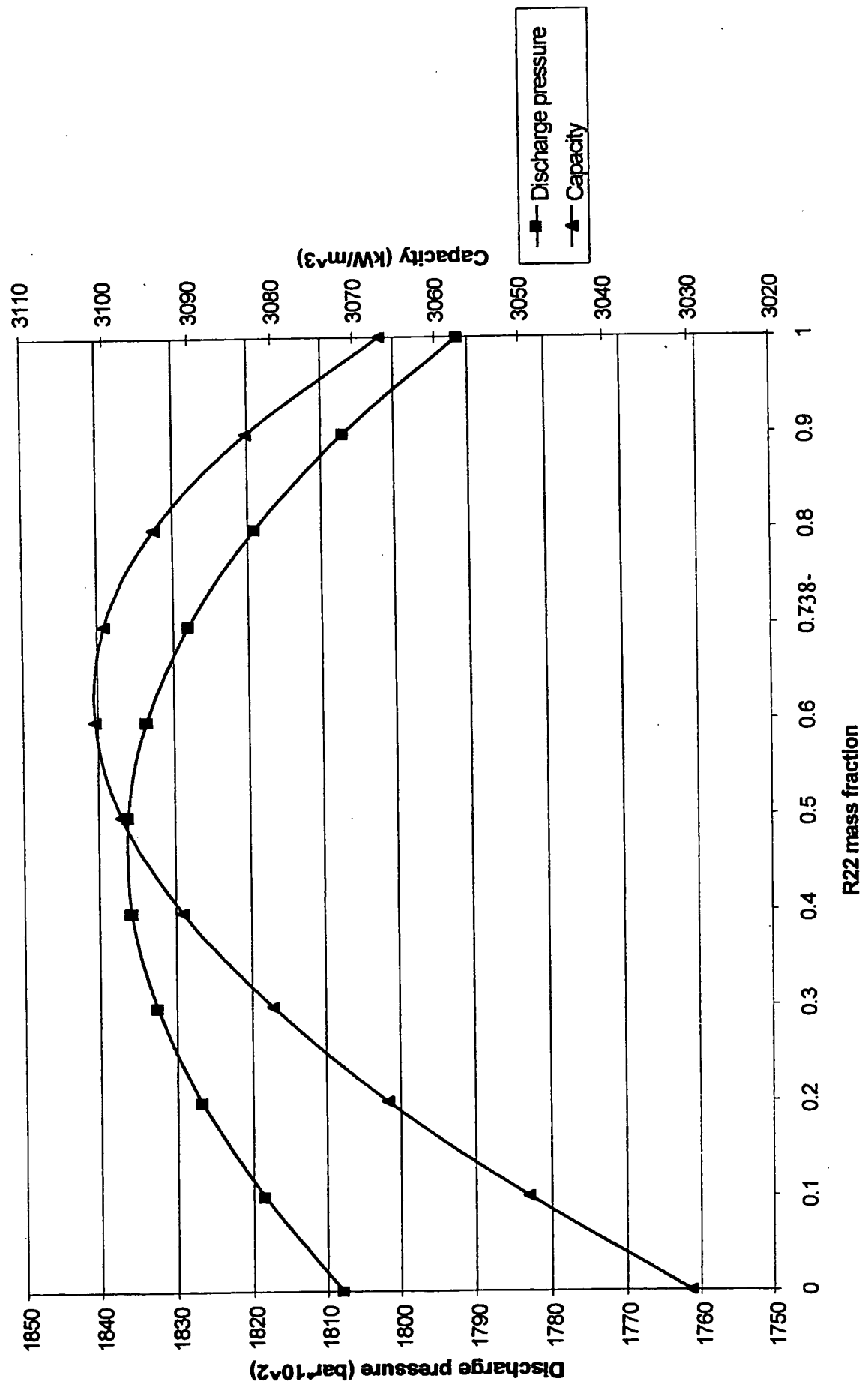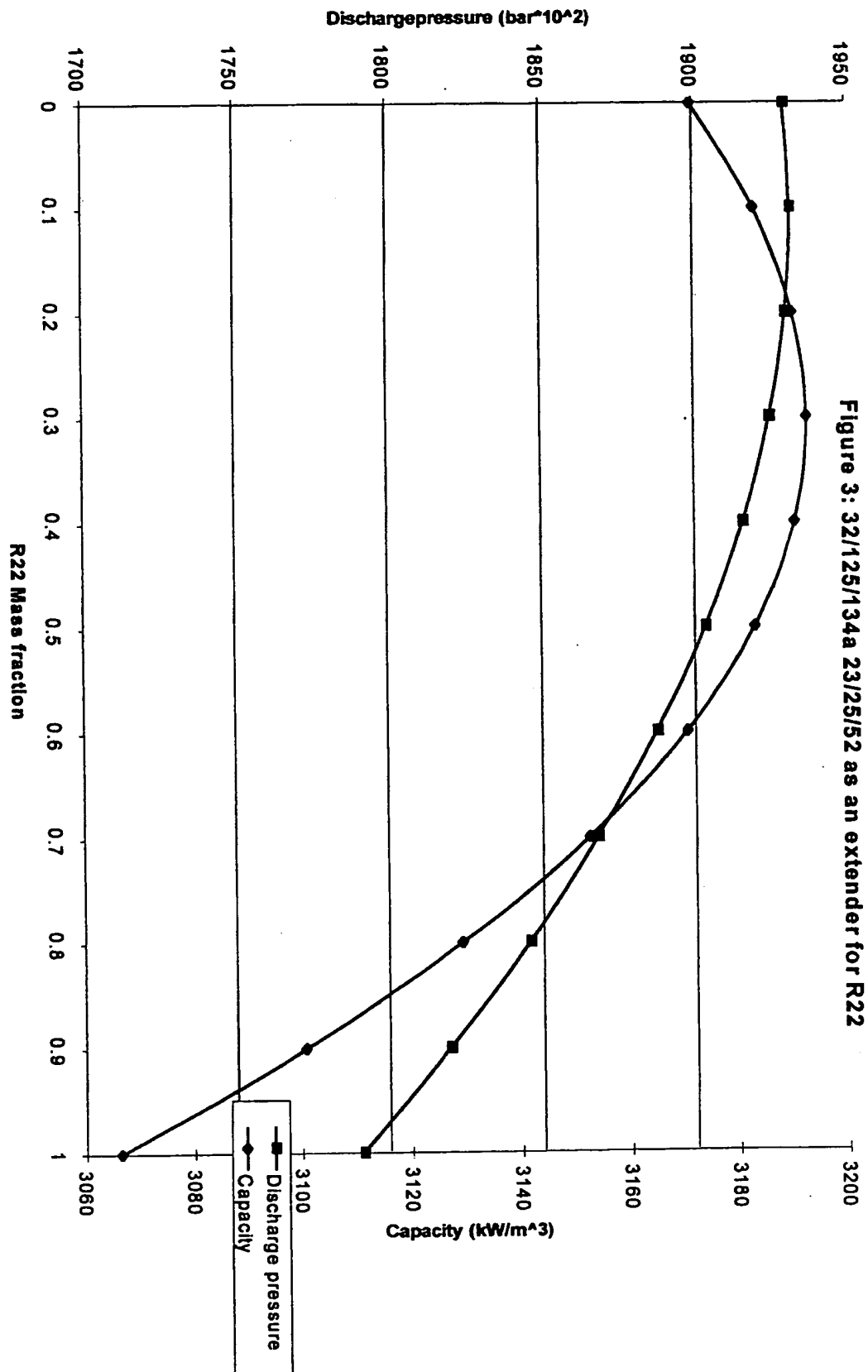OIL LEVEL MEASURED IN CENTIMETRES

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Figure 1: R125/134a 64/36 and 44/56 as R22 Extenders

Figure 2: R32(30)/R134a(70) as an extender for R22

Figure 3: 32/125/134a 23/25/52 as an extender for R22

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication. where appropriate. of the relevant passages	Relevant to claim No.
P,X	WO 00 56834 A (DU PONT) 28 September 2000 (2000-09-28) page 3, line 32 –page 4, line 1; tables 3,4 ---	1-3, 5-10,13, 14,19
A	EP 0 539 952 A (MATSUSHITA ELECTRIC IND CO LTD) 5 May 1993 (1993-05-05) table 3 ---	1-19
A	EP 0 811 670 A (MATSUSHITA ELECTRIC IND CO LTD) 10 December 1997 (1997-12-10) abstract --- -/--	1-19

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 December 2000	19/12/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE ELDATA 'Online! Gesellschaft für wissenschaft-technische Information mbH; Refrigerant R407C, 1998 S. BENMANSOUR ET AL: "Vapor-liquid equilibria and densities of difluoromethane (R 32, 23 wt. %) + pentafluoroethane (R 125, 25 wt. %) + 1,1,1,2-tetrafluoroethane (R 134a, 52 wt. %) mixture (R 407C) at temperatures between 253 K and 333 K and pressures up to 20 MPa (11600 data points)" retrieved from HTTP://WWW.FIZ-KARLSRUHE.DE/ELDATA/PROPCLASS/BENS2980.HTM XP002154412 abstract ---	19
A	DATABASE WPI Section Ch, Week 199436 Derwent Publications Ltd., London, GB; Class E16, AN 1994-291153 XP002154424 & JP 06 220430 A (SANYO ELECTRIC CO LTD), 9 August 1994 (1994-08-09) abstract ---	1-19
A	EP 0 879 866 A (DAIKIN IND LTD) 25 November 1998 (1998-11-25) abstract -----	17,18

2

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0056834	A	28-09-2000	NONE		
EP 0539952	A	05-05-1993	JP	2568774 B	08-01-1997
			JP	5117643 A	14-05-1993
			DE	69207346 D	15-02-1996
			DE	69207346 T	08-08-1996
EP 0811670	A	10-12-1997	JP	2869038 B	10-03-1999
			JP	9324175 A	16-12-1997
			CN	1167133 A	10-12-1997
JP 6220430	A	09-08-1994	NONE		
EP 0879866	A	25-11-1998	JP	10160296 A	19-06-1998
			AU	722935 B	17-08-2000
			AU	4969097 A	22-06-1998
			BR	9707309 A	20-07-1999
			US	6058717 A	09-05-2000
			CA	2244420 A	04-06-1998
			CN	1214719 A	21-04-1999
			WO	9823703 A	04-06-1998

F... DOT/ISA/210 (patent family annex) (July 1992)